

Influence of adsorption–desorption phenomena on pesticide run-off from soil using simulated rainfall

Véronique Gouy,¹ Jeanne-Chantal Dur,² Raoul Calvet,³ René Belamiet¹ and Véronique Chaplain^{2*}

¹ Division qualité des eaux, Cemagref, 3 bis quai Chauveau 69339 Lyon Cedex France

² Unité de Phytopharmacie et Médiateurs Chimiques INRA Route de Saint-Cyr 78026 Versailles Cedex France

³ Unité de Science du sol INRA INAPG 78850 Thiverval-Grignon Cedex France

Abstract: The surface run-off of a number of pesticides (diuron, isoproturon, atrazine, alachlor, acetonifene, trifluralin, lindane and simazine), chosen for their range of adsorption behaviours, was studied using simulated rainfall applied to small plots over a short time (one hour). Pesticides were applied together onto bare soil using two different sandy loam soils from Jaillière and Coet Dan sites. The surface run-off samples were collected throughout the running of the event and concentrations of pesticides were measured in both liquid and solid phases. Sorption isotherms for isoproturon and diuron on Jaillière soil as well as eroded particles were measured under equilibrium conditions and compared to their partitioning during surface run-off.

At the rainfall intensity used, both soils generated a large load of eroded particles. The average run-off flow rate increased with time for the Jaillière soil, while it remained relatively constant at a higher level for the Coet Dan soil. The concentrations of each pesticide in the run-off samples decreased as the experiments proceeded. The pesticides were classified into two types by their partitioning between the solid and liquid phases. Atrazine, simazine, diuron, isoproturon and alachlor were mainly transported in surface run-off water. By contrast, 90% of trifluralin and acetonifene was adsorbed onto eroded particles. Lindane was intermediate, with a 37% adsorption level. When the contribution of eroded particles was minor, the agrochemical concentrations were inversely proportional to the water flow rate. We have proposed a model that describes the mass of chemicals extracted from soil into surface water during a surface run-off event of a given average duration and flow rate. This model takes into account the dilution of the soil solution and the desorption of chemicals through two parameters called, respectively, the dilution factor and the extraction retardation factor. The desorption kinetic was the limiting step in the surface run-off of weakly sorbed chemicals, such as isoproturon.

© 1999 Society of Chemical Industry

Keywords: risk assessment; pesticides; run-off; adsorption; rainfall simulation; soil

1 INTRODUCTION

The use of pesticides is responsible for significant background contamination of surface waters. In many cases, the highest concentrations of pesticides are correlated with the first significant rainfall after application.^{1–3} The processes involved in such rapid pesticide transfer have not yet been elucidated. Better understanding is required to improve risk assessment.

Mechanisms involved in pesticide surface run-off are very complex and include: (i) water flow on the soil surface, which is not homogeneous but rather characterised by rills and inter-rills; (ii) pesticide

extraction from soil to the surface run-off stream; (iii) contribution of eroded particles. Hydrodynamic aspects will not be discussed here; we focus rather on points (ii) and (iii). Pesticide extraction is a general term which simultaneously refers to: (i) diffusive and convective transport from soil pores to surface run-off water; (ii) desorption from soil particles into the moving liquid boundary; (iii) dissolution of stationary pesticide particulates; (iv) transport of pesticide particulates and subsequent dissolution.⁴ The relative contributions of each process are difficult to evaluate and depend on the soil, the chemicals involved and formulation.

* Correspondence to: Véronique Chaplain, Unité de Phytopharmacie et Médiateurs Chimiques INRA, Route de Saint-Cyr, 78026 Versailles Cedex, France
E-mail: chaplain@versailles.inra.fr

† Deceased.

Contract/ grant sponsor: AIP "Ecopol".

(Received 6 March 1998; revised version received 4 June 1998; accepted 17 September 1998)

Due to the complexity of these processes, studies conducted on field-size watersheds under natural rainfall conditions often give large fluctuations in time of the pesticide concentrations in surface run-off. Leonard⁵ has, however, reported a strong correlation between surface run-off concentrations, including water and sediments, and pesticide concentrations in the surface 10 mm of watershed soil. In contrast, experiments conducted on small plots using simulated rainfall show more idealised behaviour. The pesticide concentration varies continuously with time even if these concentrations are higher than those measured under natural conditions.⁶

Run-off models are usually based on the definition of an 'active zone' interacting with run-off. Instantaneous and reversible equilibrium is assumed, so that the pesticide concentration in the soil solution can be computed from the partition coefficient K_d often used in its normalised form ($K_{oc} = K_d/oc$, where oc is the fraction of organic carbon present in the soil). The sorption constant, K_{oc} , is roughly estimated either from water solubility or, better, octanol/water partition coefficient or measured for each soil/pesticide combination using the batch technique under conditions of equilibrium. Once the depth of the mixing zone has been conveniently fixed (often chosen to be 10 mm), an adjustable parameter called the 'extraction ratio' is introduced in models to approximate the effective mass ratio of the interacting soil to water in the run-off stream. However, this parameter depends on soil properties, rainfall intensity and surface run-off rate and thus limits the predictive feature of models. Furthermore, non-linearity of isotherm curves and hysteresis in desorption experiments have often been demonstrated but are not taken into account in models. The contribution of colloidal particles to pesticide transfer is also ignored.

As described by Gouy & Belamie,⁷ theoretical predictions from the CREAMS sub-models⁸ did not agree with experimental data provided by rainfall simulation. It was suggested that the K_d value, which was measured under equilibrium conditions, did not accurately reflect the dynamic processes occurring during run-off.

The importance of associated colloid transport in pesticide transfer depended on the chemicals and events. However, contradictory results are reported in the literature. The impact of sediments appeared

small for pesticides of water solubility below 2 mg litre⁻¹.⁹ Recently, however, Munoz¹⁰ has observed a linear relationship between the loads of sediments and the concentrations of various chemicals which were all more soluble than 2 mg litre⁻¹. Other authors have reported that strongly adsorbed chemicals, characterized by K_d greater than 1000 ml g⁻¹, were mainly transported in association with colloids.^{11,12} Fawcett *et al*¹³ distinguished between three classes of agrochemicals according to their values of K_d , and postulated that molecules with K_d greater than 100 were mainly transported in run-off by sorption onto eroded particles.

Further research is thus required to evaluate the importance of kinetics in adsorption-desorption processes and the role of colloidal particles in pesticide transfer. The specific goal of our research was to achieve a better understanding of mechanisms involved in pesticide extraction from soil into the surface run-off stream. To reach this goal, we followed the surface run-off of various pesticides under controlled conditions provided by a rainfall simulator. Experiments were performed on very small plots of two soil types over a short time in order to reveal the mechanism of extraction. Partition of each pesticide between the run-off water and eroded particles was measured. The different pesticides were chosen to represent a large range of values of water solubility and partition coefficient K_{oc} . Pesticides were simultaneously applied onto the surface of bare soil in order to compare their behaviour under identical hydrodynamic conditions.

2 MATERIALS AND METHODS

2.1 Soils

Two sandy loam soils over schist were collected near Nantes (La Jaillière) and near Rennes (Coet Dan). They are representative of the north-west quarter of France and contain 2 and 2.5% (w/w) of organic matter, respectively. The Jaillière soil had sand, silt and clay fractions comprising respectively 50, 20 and 2.5% w/w.

2.2 Pesticides applied

Non-ionising pesticides were chosen and their physicochemical characteristics are given in Tables 1 and 2. Compounds were applied as commercial suspen-

Table 1. Total amounts of pesticide in run-off samples and their distribution between the sediment and liquid phases for the Jaillière experiment

Pesticide	Water solubility (mg litre ⁻¹)	K_{oc}^a (ml g ⁻¹)	Total amount in % of applied	Distribution in run-off	
				On sediment	In solution
Atrazine	33	100	3.8	0.1	3.7
Isoproturon	70	155	2.98	0.08	2.9
Diuron	42	480	1.5	0.1	1.4
Aclonifen	1.4–2.5	8800	1.5	1.4	0.1

^a AGRITOX data base.

Table 2. Total amounts of pesticide in run-off samples and their distribution between sediment and liquid phases for the Coet Dan experiment

Pesticide	Water solubility (mg litre ⁻¹)	K_{oc}^a (ml g ⁻¹)	Total amount in % of applied	Distribution in run-off	
				On sediment	In solution
Atrazine	33	100	13	0.8	12.2
Simazine	6	130	9	0.6	8.4
Alachlor	240	170	14	0.8	13.2
Lindane	7	1100	17	6.	11.
Trifluralin	1	8000	14	12.6	1.4

^a AGRITOX data base.

sion concentrate formulations to Jaillière soil: Novex flo 80 (Calliope) for diuron, Quartz GT (Rhône Poulenc) for isoproturon, Atraphyt EL (Sipcam P) for atrazine and Challenge 600 (Rhône Poulenc) for acetonifin. Unformulated trifluralin, atrazine, simazine, lindane and alachlor were applied onto Coet Dan soil. Analytical-grade compounds (Cluzeau Info Labo, Ste-Foy-La-Grande, France) with a purity of at least 98% were used for validation of our analytical methods. Radiolabelled products [*carbonyl*-¹⁴C] diuron and [*carbonyl*-¹⁴C]isoproturon were used for batch adsorption studies. They were synthesised in the laboratory with 99% radiochemical purity and specific activities were 309 and 337 MBq mmol⁻¹, respectively.

2.3 Rainfall simulation apparatus

A rainfall simulator was developed to obtain low rainfall intensity.^{14,15} This device was composed of three parts:

- (1) A pierced sprinkling tank equipped with 166 capillary rubber tubes (6 cm long × 0.5 mm internal diameter). The rain was controlled by a variable volume pump. The rainfall height was 3 m.
- (2) A 0.33 m² receiving tank (receptor) containing a 12-cm-thick layer of homogenised soil and inclined at 7%. The lower side was pierced along a horizontal line at a height of 12 cm to collect run-off samples in a receiving gutter.
- (3) A percolator tank below the soil-filled tank containing coarse sand to collect percolated water samples.

Pesticides were applied onto the bare soil surface. The initial soil moisture contents were 30 and 40% (w/w) and the applied doses of active ingredients were 150 mg m⁻² and 55 mg m⁻² for Jaillière and Coet Dan soil, respectively. The simulated rainfall of intensity 33 and 44 mm h⁻¹ respectively, began 20 h after application and surface run-off samples were collected at intervals over the hour of irrigation. After collection, run-off samples were stored at 4°C for up to 24 h. Separation of solid and liquid phases was carried out by means of continuous centrifugation (Centrifuge CEPA, Bioblock Scientific at 45 000g for 15 min and the concentration of eroded particles C_p (g litre⁻¹) was measured. The granulo-

metric distribution of eroded particles was then determined.

2.4 Extraction and pesticide analysis

Five hundred millilitres of the liquid phase was extracted using dichloromethane (3 × 50 ml). The organic phase was concentrated under light vacuum, dissolved in toluene (1 ml), applied onto a florisil cartridge and eluted by toluene + ethyl acetate (50 + 50 by volume, 25 ml) for purification. After reduction to dryness, pesticide was dissolved in isooctane for GC analysis or in water + acetonitrile (50 + 50 by volume) for HPLC analysis.

The solid phase was extracted using acetone (2 × 100 ml). The organic phase was reduced to 50 ml and transferred to a separating funnel containing pure water (450 ml). This mixture was extracted with dichloromethane (3 × 50 ml). The organic solvent was completely evaporated and pesticide was dissolved in toluene (1 ml). The purification step was performed as described above.

The solution pesticide concentration C_s (µg litre⁻¹) and adsorbed pesticide concentration Q_s (µg g⁻¹) were measured by CPG or HPLC analyses according to multi-residue methods defined by Cemagref Laboratory. Quantitative analyses were made using an electron-capture detector for trifluralin acetonifin, alachlor and lindane and using a thermionic specific detector for atrazine in the Coet Dan simulation and for simazine analyses. HPLC coupled with UV detector was used for quantitative analyses of diuron and isoproturon as well as for atrazine in the case of the Jaillière simulation. Analytical-grade compounds were used to validate analytical method. Recovery was close to 100% for each compound. It was always greater than 90%, except for lindane, for which recovery was 70%.

Gas chromatography analysis used a Varian 3400 device and an automatic injector 8200 equipped with an ECD detector (source ⁶³Ni). The temperature detector was 300°C (injector 250°C), and the injected volume was 1 µl. The column was 30 m × 0.32 mm × 0.50 µm non-polar (JW, DB608). The oven temperature program was: initial temperature 50°C held for 1 min, 20°C min⁻¹ up to 150°C, 10°C min⁻¹ up to 280°C, held for 20 min. The carrier gas was nitrogen with a flow rate of 1.5 ml min⁻¹ at 50°C.

When the thermionic specific detector was used, the temperature of the detector was 270°C, the flow rate of hydrogen was 4 ml min⁻¹ and air 175 ml min⁻¹. The temperature of the injector was 260°C and the injected volume was 1 µl. The column was 30 m × 0.32 mm × 0.25 µm non-polar (JW, DB1). The oven temperature program was: initial temperature 100°C held for 1 min, 10°C min⁻¹ up to 200°C, 5°C min⁻¹ up to 250°C, 10°C min⁻¹ up to 320°C. The carrier gas was nitrogen with a flow rate of 1.5 ml min⁻¹ at 50°C.

HPLC analysis used a Kontron device fitted with a guard-column of Lichrospher 60 RP Select B type (4 mm × 4 mm) and an analytical column of Lichrospher 60 RP Select B type (250 mm × 4.6 mm). Elution with acetonitrile + water proceeded at 1 ml min⁻¹ with an isocratic pump; elution began with 28 + 72 by volume for 28 min, followed by an increase to 68 + 32 by volume over 10 min, an increase to 90 + 10 by volume over 5 min, and a stationary phase during 5 min. UV absorbance was monitored at 224 nm for atrazine analysis and 245 nm for diuron and isoproturon.

The values of the detection limit in liquid and solid phase were respectively 0.03 µg litre⁻¹ and 10 µg kg⁻¹ for aclonifen, 0.52 µg litre⁻¹ and 3 µg kg⁻¹ for atrazine in Jaillièrè, 0.5 µg litre⁻¹ and 0.5 µg kg⁻¹ for diuron, 0.11 µg litre⁻¹ and 0.5 µg kg⁻¹ for isoproturon, 0.08 µg litre⁻¹ and 30 µg kg⁻¹ for alachlor, 0.5 µg litre⁻¹ and 70 µg kg⁻¹ for atrazine in Coet Dan, 0.02 µg litre⁻¹ and 20 µg kg⁻¹ for lindane, 0.5 µg litre⁻¹ and 50 µg kg⁻¹ for simazine, 0.05 µg litre⁻¹ and 20 µg kg⁻¹ for trifluralin.

2.5 Adsorption isotherms

Twenty grams of sieved (<2 mm) air-dried soil particles were mixed in a glass bottle with 20 ml of diuron or isoproturon solutions of variable initial concentrations, C_i , in 0.01 M CaCl₂. The initial concentration range was 0.1, 0.5, 1 and 5 mg litre⁻¹ for both compounds. All the pesticides used were radiolabelled. The initial radiolabelled pesticide solution was such that the activity in the batches was 200 Bq ml⁻¹. Samples were mixed on a rotary shaker at room temperature for 24 h. After decanting, the supernatant solution was centrifuged, radioactivity was determined by scintillation counting using a Wallac 1409 scintillation apparatus and the equilibrium concentration (C_e) was derived. The amount, Q_e (mg g⁻¹) of pesticide sorbed was calculated using the relation

$$Q_e = (C_i - C_e) \cdot V/m$$

where V was the volume of solution (litre) and m the mass of soil (g).

Two replicates were used for each sample and checked with a blank (a volume V of aqueous pesticide solution without soil). Experimental error was

estimated to lie within a range of 2 to 5% of quantitative results.

The Freundlich model

$$Q_{\text{ads}} = K_f C_e^{1/n}$$

was applied to each isotherm curve. Adsorption measurements on sediments differed only in their particle concentration of 7.2 g litre⁻¹. Additional adsorption measurements were performed with a concentration of Jaillièrè soil of 10 g litre⁻¹, which was close to the concentration of sediments in run-off water samples.

3 RESULTS

3.1 Pesticide surface run-off during rainfall simulation

3.1.1 Pesticide transfer in run-off water

An average flow rate F_w was derived for each run-off sample from the volume collected during the time step Δt . This average value continuously increased with time for the Jaillièrè experiment and was constant for the Coet Dan experiment over the 15 min of surface run-off (Fig 1). Values reached in the latter soil were relatively large, greater than 200 ml min⁻¹ corresponding to a intensity of 36 mm h⁻¹.

Over the same period, average concentrations, C_s , of each pesticide measured in the liquid phase of each run-off sample decreased with time due to a dilution effect (Fig 2). The ratio of the concentration of the two molecules also varied with time during each experiment, indicating that a dynamic process

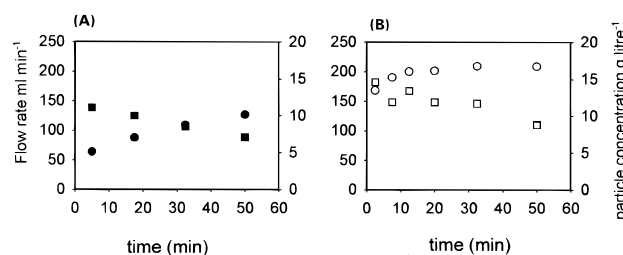


Figure 1. Variation in the average run-off flow rate (○, left y-axis) and average particle concentration (□, right y-axis) with time measured during rainfall simulation on (A) Jaillièrè soil (full symbols) and (B) Coet Dan soil (empty symbols).

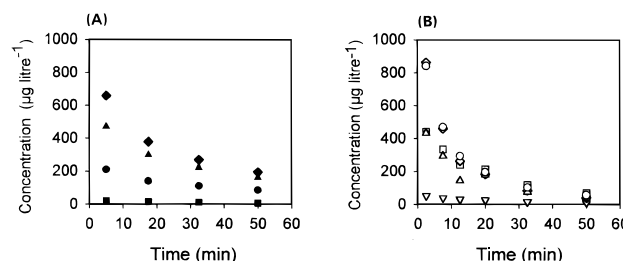


Figure 2. Average pesticide concentration in the liquid phase of run-off samples for each time step. (A) Jaillièrè soil (● diuron, ▲ isoproturon, ▲ aclonifen, ■ atrazine and (B) Coet Dan soil (▽ trifluralin, □ lindane, ◇ atrazine, △ simazine, ○ alachlor).

was also involved in pesticide transfer. The highest concentrations (greater than $500 \mu\text{g litre}^{-1}$) were recorded at the beginning of the experiment with atrazine, isoproturon and alachlor and to lesser degree with simazine, diuron and lindane. Trifluralin on Coet Dan soil and aclonifen on Jailli re were distinguished from other pesticides by low concentrations (below $100 \mu\text{g litre}^{-1}$). Both these pesticides have low solubility in water and a large partition coefficient (see Tables 1 and 2). Furthermore, the temporal variations in the concentration of trifluralin were small (from 51 to $10 \mu\text{g litre}^{-1}$) compared to variations recorded over the same time with others compounds. Indeed the concentrations of simazine, alachlor and atrazine decreased by factors of 10, 15 and 21, respectively. In contrast, the decrease of the C_s values of aclonifen, from 20 to $6 \mu\text{g litre}^{-1}$, was greater than those recorded for weakly sorbed compounds, indicating that our results cannot be extended over different soils but are specific to our experimental conditions.

3.1.2 Pesticide transfer associated with eroded particles

Suspended soil particle concentrations, C_p , decreased with time (Fig 1), and were greater in the Coet Dan experiment than in the Jailli re soil, ranging respectively from 14.5 to 9 g litre^{-1} and from 11 to 7 g litre^{-1} . This difference was attributed to the higher rainfall intensity and, thus, higher surface run-off flow rate in the Coet Dan experiment, rather than to any difference in the properties of the soils.

Average adsorbed pesticide concentrations, Q_s , on transported particles were measured for each run-off sample (Fig 3). We distinguished between two classes of pesticides. The first was characterised by low values of Q_s ($< 2 \mu\text{g g}^{-1}$) which were practically constant over time; these included atrazine, simazine, alachlor, diuron and isoproturon, with the first three behaving very similarly (Fig 3B). The second class, including aclonifen and trifluralin, showed high values of Q_s , from 10 to $34 \mu\text{g g}^{-1}$, and large variations with time, especially soon after initiation of run-off. These two classes also had differing amounts of pesticide transported on colloids, with

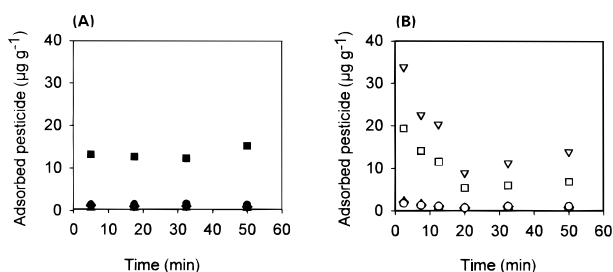


Figure 3. Variation with time of the concentration of adsorbed pesticide on sediment particles. (A) Jailli re soil (●) diuron, (▲) isoproturon, (■) aclonifen, (◆) atrazine and (B) Coet Dan soil (▽) trifluralin, (□) lindane, (◇) atrazine, (△) simazine, (○) alachlor.

less than 10% of the total amount transported (atrazine 5.9%, simazine 8%, alachlor 5.8%, diuron 9% isoproturon 2% and atrazine 3%) in the first class and close to 90% in the second (trifluralin 89% and aclonifen 91%). Lindane showed an intermediate behaviour with 37% transported on colloids.

3.1.3 Total pesticide transfer

The total amount of herbicide found in run-off for those compounds, and transported mostly in solution was correlated to the K_d values. Isoproturon and atrazine were transported to a similar degree in the Jailli re experiment and atrazine and alachlor in the Coet Dan experiment. Most sorbed or less-soluble compounds, such as diuron and simazine, were still transported in solution, but the loss was lower. This indicated that the loss was related to the pesticide concentration of the soil solution. The lower solubility in water of simazine is a possible explanation of such a difference, but more soil-specific adsorption data together with replicated simulations are required to confirm this assumption.

For compounds transported mostly in association with colloids, the partition coefficient (K_{oc}) was insufficient to determine the amount of pesticide lost in run-off. Indeed, the amounts of diuron and aclonifen transported from Jailli re soil were very similar (equal to 1.5% of applied) even though the two molecules are characterised by very different values for K_{oc} (Table 1). Similar effects occurred on the Coet Dan soil with trifluralin and alachlor.

3.2 Equilibrium reactivity of soil and eroded particles

3.2.1 Characterisation of eroded particles

Particles eroded from the Jailli re soil were collected in a single run-off sample by applying artificial rain onto the bare soil surface (without first applying pesticide) for one hour. Their size distribution was clay 20, silt 78, sand 1.1 and coarse sand 0%. No particles with a size greater than 2 mm were transported in surface run-off waters, and only a small fraction (1.1% w/w) had a diameter greater than $50 \mu\text{m}$. In contrast, the silt and clay fractions in sediments were increased by factors of 3.9 and 8.3 respectively, compared with the parent soil.

Sediment was also enriched in total organic carbon by about 1.8 times for both soils. However, the enrichment progressively increased with time from 2.4 to 3.2% w/w in the Jailli re experiment whilst it decreased from 5.4 to 4.0 in the Coet Dan case. The concentration of dissolve organic carbon was small, representing only 1.5% of the organic carbon in the sediments. The pH of run-off water was close to 7, corresponding to the pH of the applied water.

3.2.2 Adsorption isotherms

The concentration of particles eroded from Jailli re soil was large enough (7.2 g litre^{-1}) to allow adsorption isotherm measurements. Isoproturon was

adsorbed less than diuron in soil (Fig 4A) as observed elsewhere.^{16,17} The Freundlich model leads to an exponent in soil close to unity, with the partition coefficients K_d derived from these linear isotherms being 6.4 and 1.6 g litre⁻¹ for diuron and isoproturon, respectively. In contrast, both molecules were adsorbed to a similar extent on eroded particles, for which the Freundlich exponent was close to 0.7 for both molecules (Fig 4A). As particle concentration might influence adsorption results,¹⁸ measurements were also performed for diuron on soil suspensions diluted to 10 g litre⁻¹. They showed little change in K_d , which increased slightly to 8.3 g litre⁻¹. Thus, the discrepancy between soil and sediments observed under conditions of equilibrium reflects a change in the surface reactivity of soil as compared to eroded particles, which may be attributed to sediment enrichment in fine particles and organic matter.

3.3 Partition of pesticides during surface run-off

3.3.1 Diuron and isoproturon

Partition of diuron and isoproturon between eroded particles and the liquid phase was described by the variation in the ratio of the concentration Q_s of chemical adsorbed to sediments to the aqueous concentration, C_s , measured at each time step during the Jailli re experiment (Fig 4B). These values were quite constant (around 1.4 µg g⁻¹ and 0.6 µg g⁻¹) for diuron and isoproturon, respectively. Comparing this observation with the isotherm curves obtained for sediments using the batch technique (dotted lines in Fig 4B), adsorption equilibrium of both molecules on eroded particles was not achieved, particularly at the beginning of run-off when values of C_s were largest. Thus, in the short duration of surface run-off, adsorption on eroded particles rather than desorption into the surface run-off stream occurred for both molecules.

3.3.2 Other molecules

The concentrations Q_s are represented as a function of C_s for all compounds in Fig 5A for the Jailli re soil and Fig 5B for the Coet Dan soil. Chemicals for

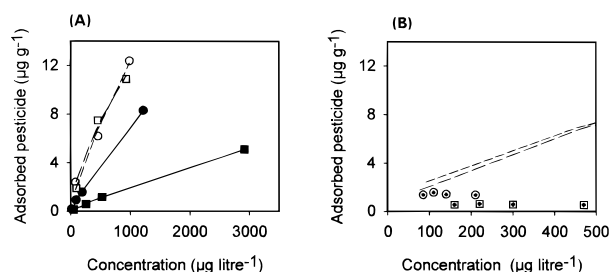


Figure 4. (A) Equilibrium adsorption isotherm curves for (●, ○) diuron and (■, □) isoproturon on (●, ■) Jailli re soil and (○, □) on eroded particles generated by the rainfall simulation. The solid and broken lines refer to the Freundlich model applied to adsorption data for soil and sediments respectively. (B) Partitioning of (○) diuron and (□) isoproturon between the water and eroded particles during run-off.

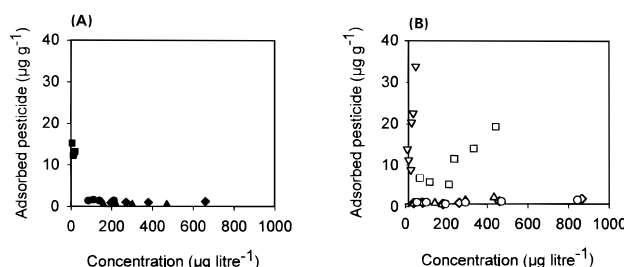


Figure 5. Partitioning of pesticides between the dissolved phase and transported colloids for each time step of the rainfall simulation with (A) Jailli re soil, (●) diuron, (▲) isoproturon, (■) atrazine, (◆) atrazine and (B) and Coet Dan soil, (▽) trifluralin, (□) lindane, (◇) atrazine, (△) simazine, (○) alachlor.

which transport essentially proceeded in solution are distinguished by their rapid decrease in C_s and their small and constant values of Q_s . This occurred for diuron and isoproturon on Jailli re soil, for simazine and alachlor on Coet Dan and for atrazine on both soils. Due to the low values of Q_s for this set of chemicals, it appears possible that equilibrium of adsorption was not being achieved in the run-off stream, just as in the case of diuron and isoproturon. Adsorption on eroded particles was limited by the short duration of surface run-off, lasting only a few minutes.

In contrast, trifluralin on Coet Dan soil and acclonifen on Jailli re soil were transported mostly on colloids. The run-off of these compounds was characterised by large values of Q_s and small values of C_s . Figure 5B shows a rapid decrease in Q_s for trifluralin along with a slight variation of C_s . The temporal variations in Q_s measured for trifluralin and acclonifen are dependent on the change in the sorptive properties of the sediments during run-off. This concentration Q_s was related to the organic content measured in run-off samples. For each molecule, values were quite constant over the time of the experiment (close to 5 µg g⁻¹ for acclonifen and 4 µg g⁻¹ for trifluralin). Furthermore, these very similar values show the importance of the organic content in sediments for retention of acclonifen and trifluralin.

4 DISCUSSION

Results obtained on Jailli re soil have indicated an inverse relationship between the amount of herbicide found in run-off samples and the partition coefficient K_{oc} for weakly adsorbed molecules of moderate water solubility (eg atrazine, isoproturon and diuron). We are now interested in the role played in pesticide transfer by the kinetics of the extraction process from soil to the run-off stream. As colloids make only a minor contribution to transport, it is expected that the run-off flow rate will have a specific effect on each compound if their kinetics differ. A linear relationship was established between the concentration C_s and the inverse of the water flow rate $1/F_w$ with good regression coefficients for diuron, isopro-

turon and atrazine on the Jaillière soil. An effective concentration C'_s was deduced by assuming that the amount of adsorbed pesticide was primarily in solution. A linear relationship was also established between C'_s and $1/F_w$ (see eqn (1) and Fig 6). The regression coefficient values were > 0.99 for diuron, isoproturon and atrazine on the Jaillière soil.

$$C'_s = \frac{a'}{F_w} - b' \quad (1)$$

Two important points must be made about this plot. Firstly, this linear relationship implies that there was a continuous extraction process that supplied the soil water with herbicides. Secondly, the slopes differed amongst compounds, due to a kinetic effect. Two fundamental extraction processes must be involved: (i) initial dissolution of formulated chemicals, (ii) desorption from soil particles. We think that desorption played the dominant role because none of these compounds was likely still to be in the formulated state.

The average mass m_i of pesticide contained in the sample (i) collected during Δt_i with an average flow rate F_{wi} can be derived from eqn (1) by the product of the average concentration $C_s(i)$ and the sample volume $V(i)$:

$$m_i(\Delta t_i) = C_s(i)V(i) = a' \Delta t_i - b' F_{wi} \Delta t_i \quad (2)$$

The first term in eqn (2) does not depend on the flow rate and is associated with the dilution of the soil water. It represents the mass of pesticide that could be extracted if the concentration in the soil water was maintained constant during the run-off event. The soil is considered as a reservoir that would allow the equilibrium concentration throughout the soil water to be achieved instantaneously. In contrast, the second term is dependent on flow rate and represents the efficiency of pesticide extraction.

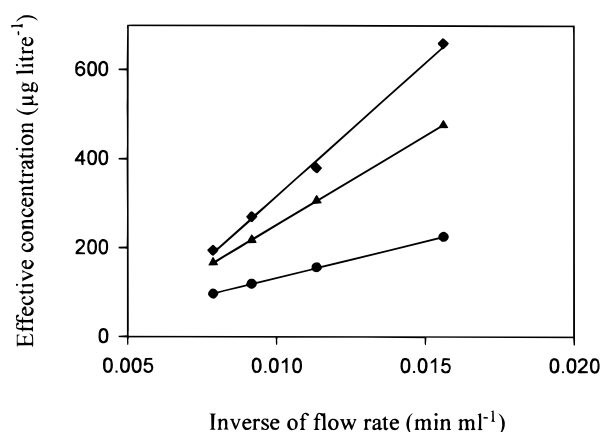


Figure 6. Variation of the effective concentration of (●) diuron, (▲) isoproturon and (◆) atrazine versus the inverse of the average run-off flow-rate in the Jaillière simulation. The effective concentration was derived by assuming that the whole mass of pesticide was initially in the liquid phase. Straight lines represent linear regressions.

This term gives the mass that must be deducted because equilibrium between solids and soil water is not instantaneous. This delaying effect is most pronounced with the least-adsorbed chemicals. Indeed, this term indicates the capacity of the soil to maintain a constant concentration. If the amount of adsorbed chemical is large (and aqueous concentration low), then the desorption of a small fraction of pesticide is required to regain equilibrium concentration following dilution. Such behaviour was observed in desorption studies carried out on undisturbed soil under static conditions.¹⁹ Equilibrium was reached quickly. It is expected that in this case the b parameter would be small, as demonstrated for diuron and isoproturon.

If surface run-off proceeds by successive steps of duration Δt_i and average flow rate F_{wi} , the total mass M of pesticide collected is:

$$M = \sum_i a' \Delta t_i - \sum_i b' F_{wi} \Delta t_i = a'T - b'V \quad (3)$$

where T is the duration of run-off and V the total volume of run-off sample. This quantity M represents the mass of pesticide extracted from the soil into the surface run-off stream. Only a proportion of M will be transported over a longer distance.

5 CONCLUSION

In this paper we have used rainfall simulation experiments to study the mechanism of loss of pesticides from soil into the surface run-off stream and the role of adsorption-desorption phenomena in this dynamic situation. Results have given us a better understanding of the behaviour of weakly sorbed chemicals. Desorption kinetics appeared to be the limiting step in the surface run-off of isoproturon and atrazine. We propose a model that describes the mass of pesticide lost from soil by surface run-off. This model distinguishes between dilution of the soil solution during surface run-off and desorption of chemicals from soil through two parameters, the dilution factor and the retardation extraction factor. These parameters are specific to each soil/pesticide combination. Additional chemicals should be used to confirm such results and to identify any determining role of water solubility. Further experiments should include replicated simulations together with a systematic comparison of the sorptive properties of soil and sediments in order to study the influence of soil properties on pesticide run-off.

ACKNOWLEDGEMENTS

This work received financial support from the AIP 'Ecopol' directed by P. Chassin. The authors would like to acknowledge C Garon-Boucher and B Laillet from the Water Quality Division of Cemagref Lyon for their analysis work. They also thank the labor-

atories of Chemistry and Ecodynamic of Sediments of Cemagref Lyon for their help. Dr P Gaillardon is thanked for helpful discussions.

REFERENCES

- 1 Patty L, Réal B and Gril JJ, The use of grassed buffer strips to remove pesticides, nitrates and soluble phosphorus compounds from runoff water. *Pestic Sci* **49**:243–251 (1997).
- 2 Belamie R and Gouy V, Introduction des polluants dans le milieu fluvial. Influence du ruissellement des sols. *Oceanis* **18**:505–521 (1992).
- 3 Carluier N Gouy V and Gril JN, Contamination des eaux de surface par des produits phytosanitaires et modélisation. *Ingénieries-EAT* **6**:19–30 (1996).
- 4 Bailey GW, Swank AR Jr and Nicholson HP, Predicting pesticide runoff from agricultural land: a conceptual model. *J Environ Qual* **3**:95–102 (1974).
- 5 Leonard RA, Movement of pesticides into surface waters, in *Pesticides in the Soil Environment: Processes, Impacts, and Modeling*, Ed by Cheng HH, Soil Science Society of America, Inc, Madison, Wisconsin, USA, pp 303–349 (1990).
- 6 Karishoff SW, Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere* **10**:833–846 (1981).
- 7 Gouy V and Belamie R, Using the CREAMS pesticides transfer sub-model at a rainfall simulation scale. *Wat Sci Tech* **28**:679–683 (1993).
- 8 Knisel WG, CREAMS, a field scale model for chemicals, runoff and erosion from agricultural management systems, Ed by Knisel WT, USDA. *Conservation Research Report*, **26** (1980) 643 pp.
- 9 Wauchope, RD., The pesticide content of surface water drainage from agricultural fields: A review. *J Environ. Qual.*, **7**:459–472 (1978).
- 10 Munoz JF, Méthodologie d'étude des produits phytosanitaires. Etude d'un bassin versant viticole : l'Ardières (Beaujolais). Mise au point de méthodes analytiques de pesticides. *Thèse de troisième cycle*, Université Claude Bernard, Lyon, France (1992) 175 pp.
- 11 Foster GR, Young RA and Neibling WH, Sediment composition for nonpoint source pollution analyses. *Transactions of the ASAE* **133**–146 (1985).
- 12 Walter MF, Stennhuis TS and Haith DA, Nonpoint source pollution control by soil and water practices. *Transactions of the ASAE* **77**:834–840 (1979).
- 13 Fawcett RS, Christensen BR and Tierney DP, The impact of conservation tillage on pesticide runoff into surface water : a review and analysis. *J Soil and Water Conservation* **126**–135 (1994).
- 14 Patty L, Limitation du transfert par ruissellement vers les eaux superficielles de deux herbicides (isoproturon et diflufenicanil). Méthodologie analytique et étude de l'efficacité de bandes enherbées. *Thèse de troisième cycle*, Université Joseph Fourier, Grenoble, France 217 pp (1997).
- 15 Gouy V, Contribution de la modélisation à la simulation du transfert des produits phytosanitaires de la parcelle agricole vers les eaux superficielles. *Thèse de troisième cycle*, Université Louis Pasteur, Strasbourg, France 315 pp (1993).
- 16 Gaillardon P and Dur JC, Influence of soil moisture on short-term adsorption of diuron and isoproturon by soil. *Pestic Sci* **45**:297–303 (1995).
- 17 Gaillardon P, Influence of soil moisture on long-term sorption of diuron and isoproturon by soil. *Pestic Sci* **47**:347–354 (1996).
- 18 Jamet P and Roche D, Influence of soil–water ratio on adsorption–desorption kinetics of isoxaben in soil, in *Fate and prediction of environmental chemicals in soils, plants and aquatic systems*, Ed by Mansour M, Lewis Publishers, USA pp 221–234 (1993).
- 19 Gaillardon P., Desorption of diuron and isoproturon from undispersed clay loam soil., *Pestic Sci* (1998). in press.